Heterogeneous Atmospheric Dust

Individual Particle Microanalysis
Optical Property Modeling
Lab-Generated Particle Analogs

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Overview

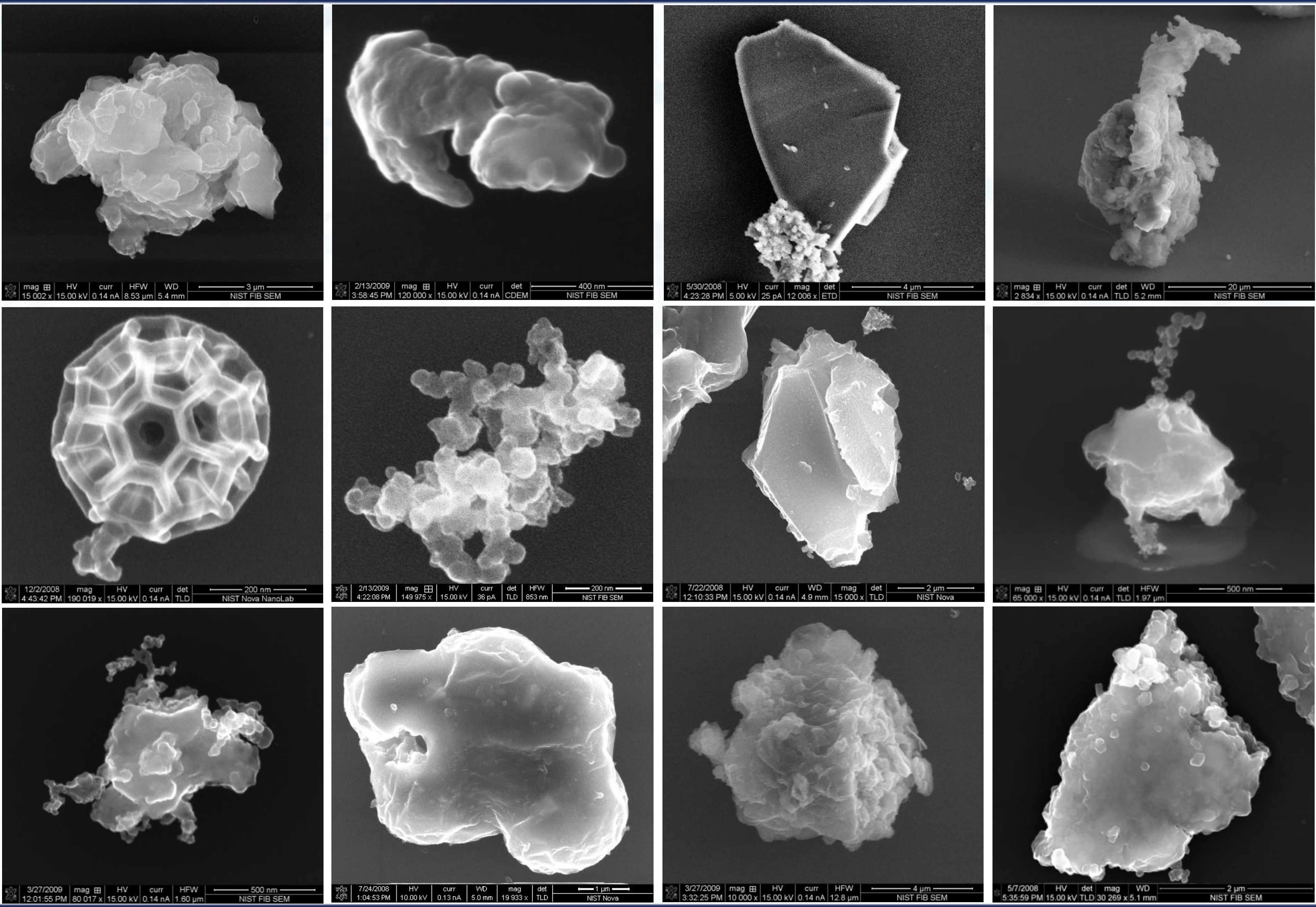
- Heterogeneous atmospheric dust:
  - Why important in climate change science
  - Goals of this research

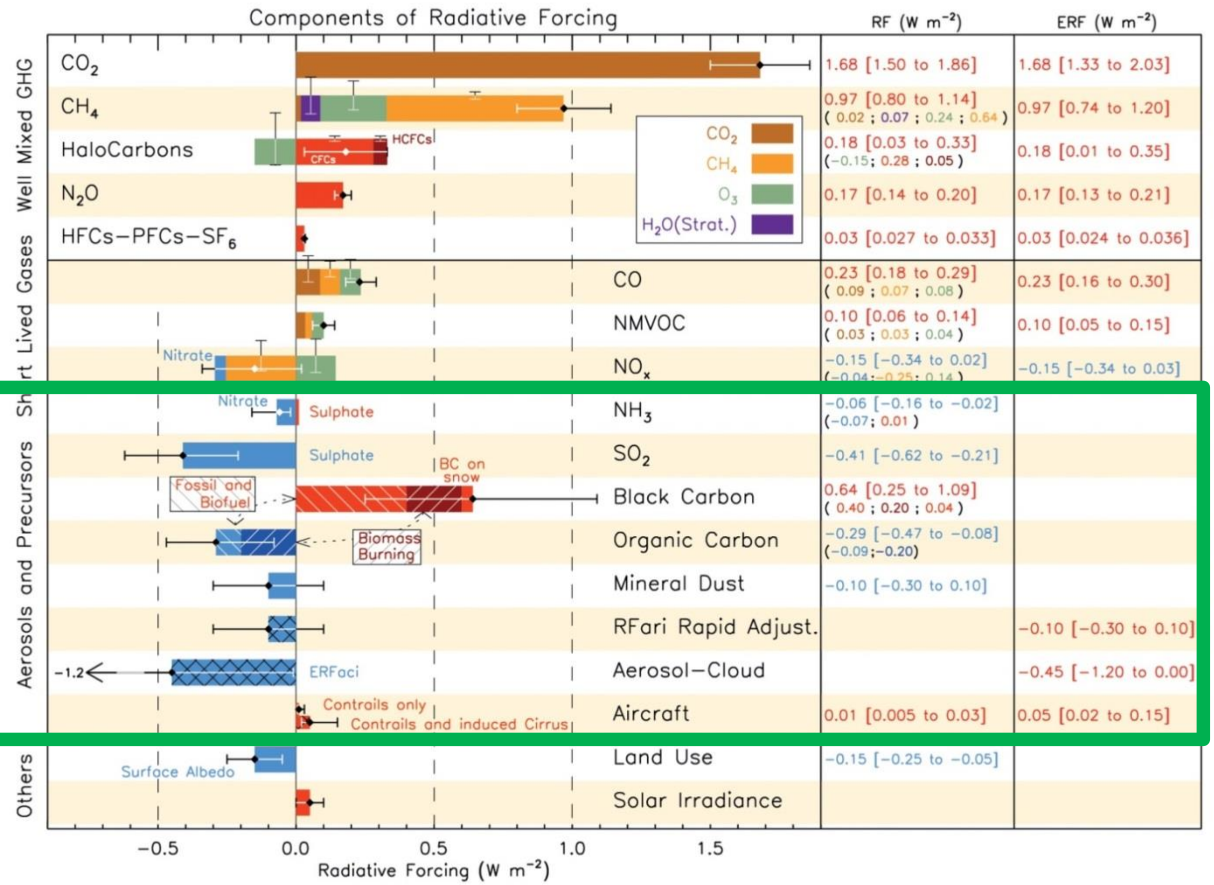
- Microanalysis of individual particles:
  - Particle size, shape, chemical composition, internal structure

- Particle 3-D spatial models from focused ion-beam tomography

- Optical property modeling (absorption and scattering) based on 3-D spatial models

- Lab-generated atmospheric particle analogs with mixed optical phases
  - Paradigm for creating suite of mixed-phase reference materials


mag HV curr HFW WD 3 µm
15 002 x 15.00 kV 0.14 nA 8.53 µm 5.4 mm NIST FIB SEM
2/13/2009 mag HV curr det 400 nm
3:58:45 PM 120 000 x 15.00 kV 0.14 nA CDEM NIST FIB SEM
5/30/2008 HV curr mag det 4 µm
4:23:28 PM 5.00 kV 25 pA 12 006 x ETD NIST FIB SEM
mag HV curr det WD 20 µm
2 834 x 15.00 kV 0.14 nA TLD 5.2 mm NIST FIB SEM
12/2/2008 mag HV curr det 200 nm
4:43:42 PM 190 019 x 15.00 kV 0.14 nA TLD NIST Nova NanoLab
2/13/2009 mag HV curr det HFW 200 nm
4:22:08 PM 149 975 x 15.00 kV 36 pA TLD 853 nm NIST FIB SEM
7/22/2008 HV curr WD mag det 2 µm
12:10:33 PM 15.00 kV 0.14 nA 4.9 mm 15 000 x TLD NIST Nova
mag HV curr det HFW 500 nm
65 000 x 15.00 kV 0.14 nA TLD 1.97 µm
3/27/2009 mag HV curr HFW 500 nm
12:01:55 PM 80 017 x 15.00 kV 0.14 nA 1.60 µm NIST FIB SEM
7/24/2008 HV curr WD mag det 1 µm
1:04:53 PM 10.00 kV 0.13 nA 5.0 mm 19 933 x TLD NIST Nova
3/27/2009 mag HV curr HFW 4 µm
3:32:25 PM 10 000 x 15.00 kV 0.14 nA 12.8 µm NIST FIB SEM
5/7/2008 HV det mag WD 2 µm
5:35:59 PM 15.00 kV TLD 30 269 x 5.1 mm NIST FIB SEM

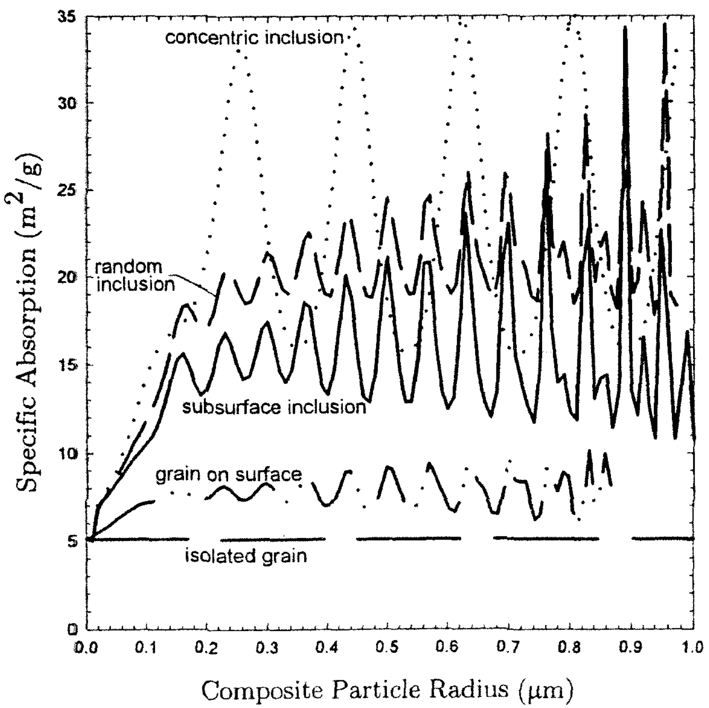


IPCC AR5, The Physical Science Basis, 2013

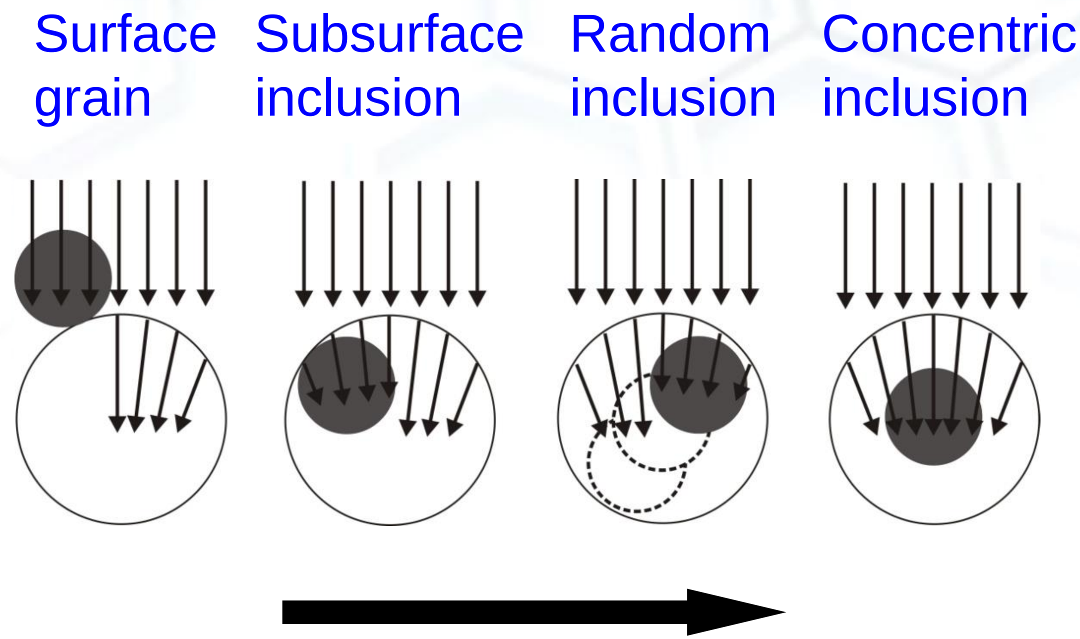
What's missing:

- Urban dust
- Aged aerosols (e.g., Asian pollution and dust transported to Hawaii)
- → Heterogeneous aerosols

Light Absorption in Internally-Mixed Particles



Fuller et al., *J. Geophys. Res.* 104 (1999) 15,941-15,954 (Figure 12)



Increasing specific absorption (α_a)

Research Goals

- **Determine the extent of <u>natural variation</u> in optical properties of heterogeneous particles (scattering and absorption efficiencies) based on optical models of <u>selected</u> individual particles**

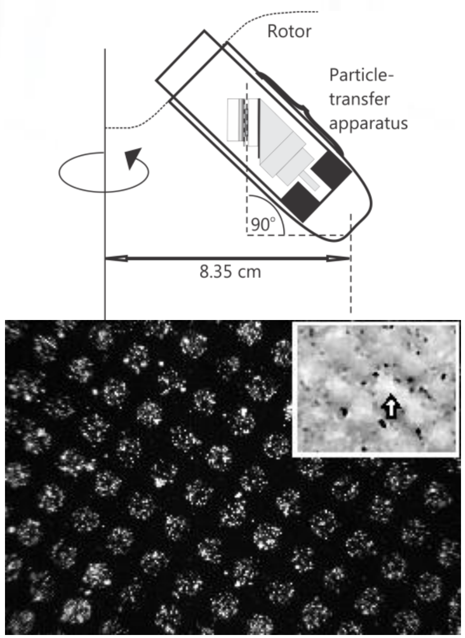
- **Determine differences in optical properties with respect to**
    - Season
    - Geographic region (U.S. East, West, South)
    - Development (urban vs. rural)
    - Continental air vs marine air

- **Generate optically heterogeneous particles in the lab as analogs of real heterogeneous particles**

Microanalysis Process

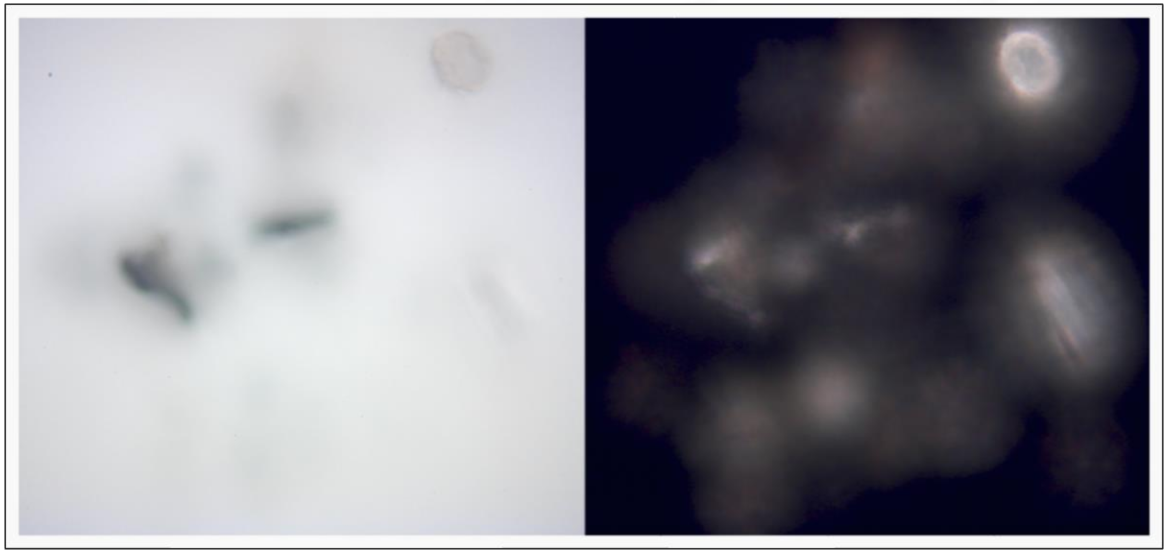
- Sample preparation
- Survey of optical behavior → Light microscopy
- Particle population analysis → Automated SEM
- Individual particle SEM analysis → X-ray spectroscopy, electron backscatter diffraction

Particle Transfer:
Filter to germanium wafer

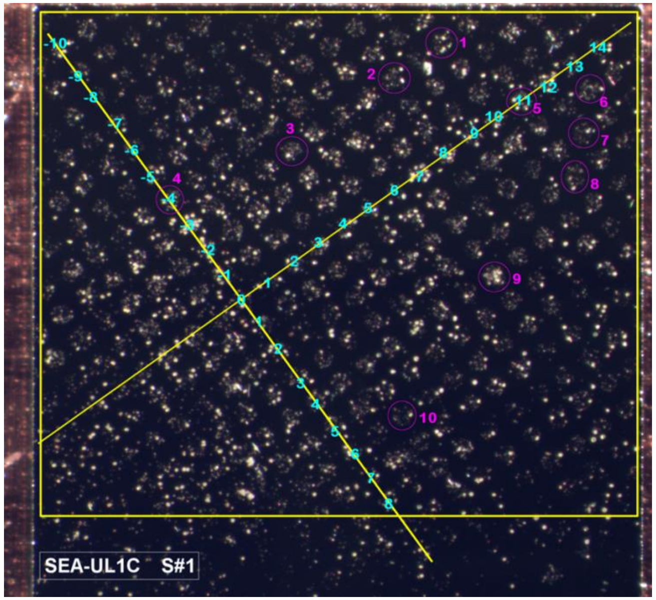


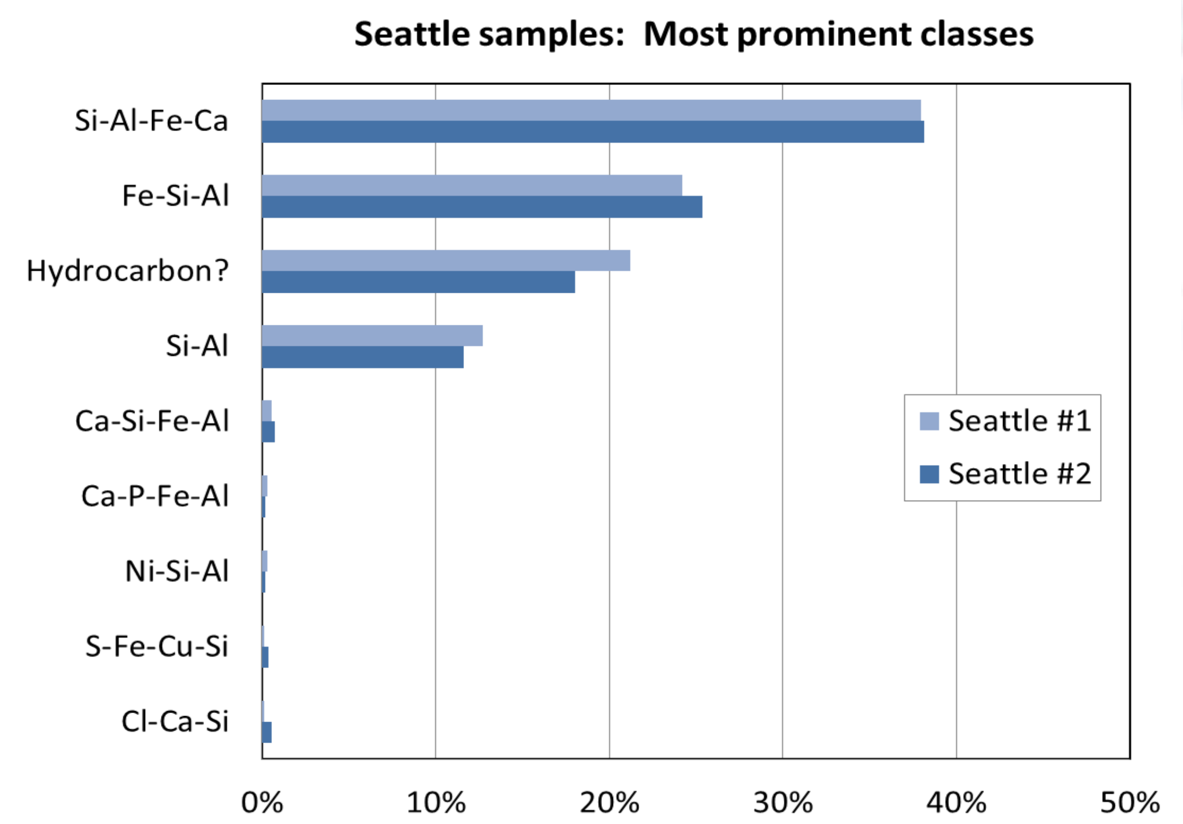
Light Microscopy: Seattle Winter 2005 Sample

Bright Field Dark Field

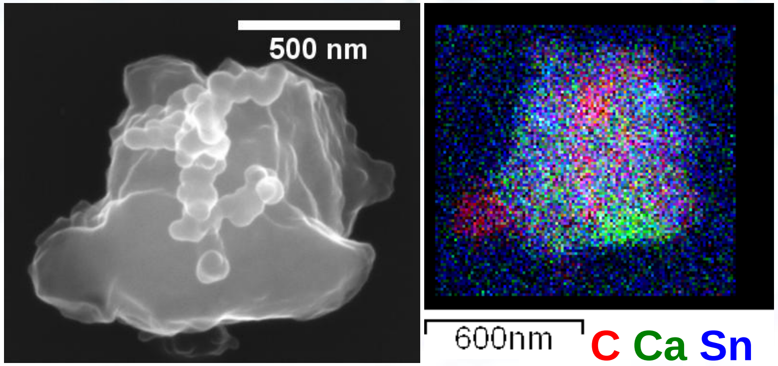


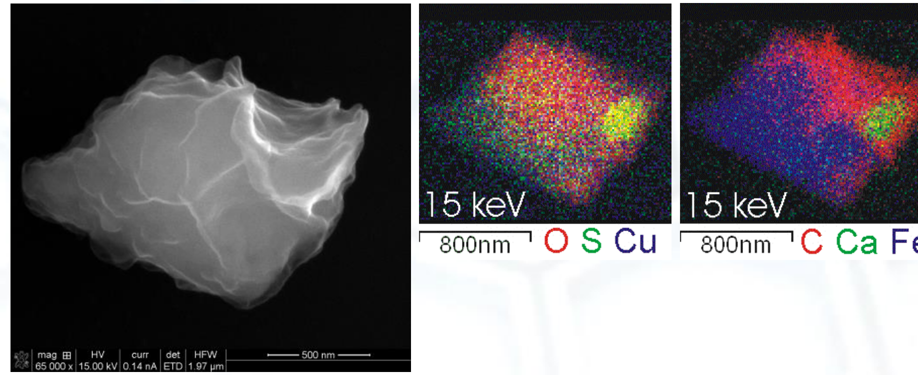
Analysis of Particle Populations

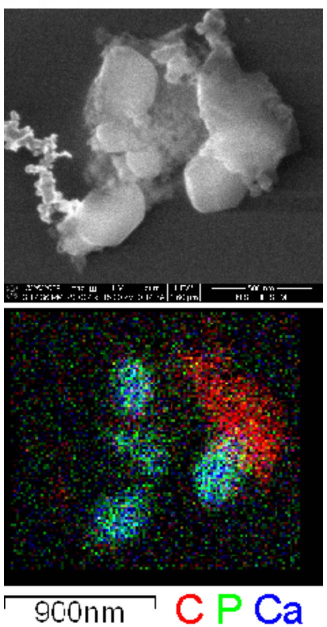


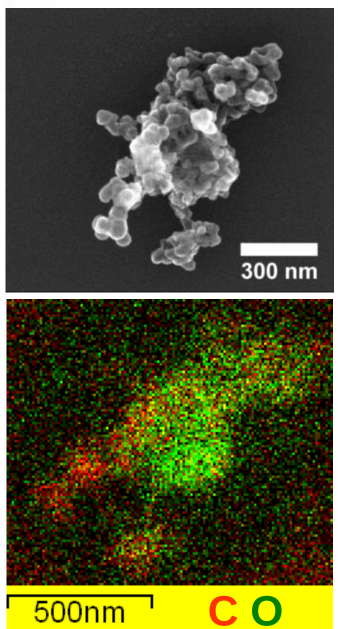


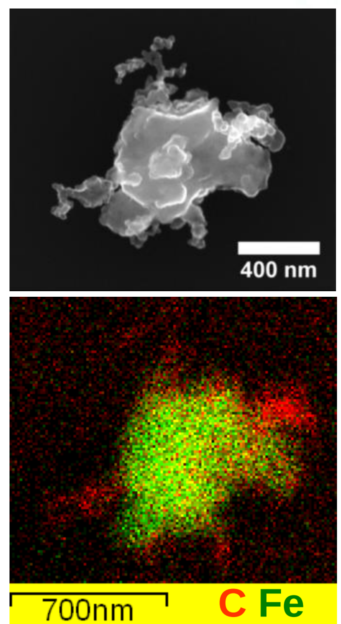
Complexity of Urban Particles: Natural or Anthropogenic?

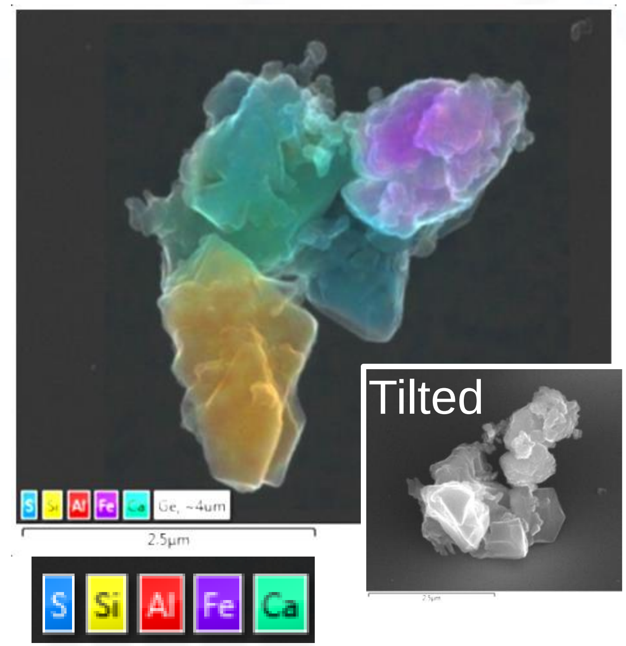




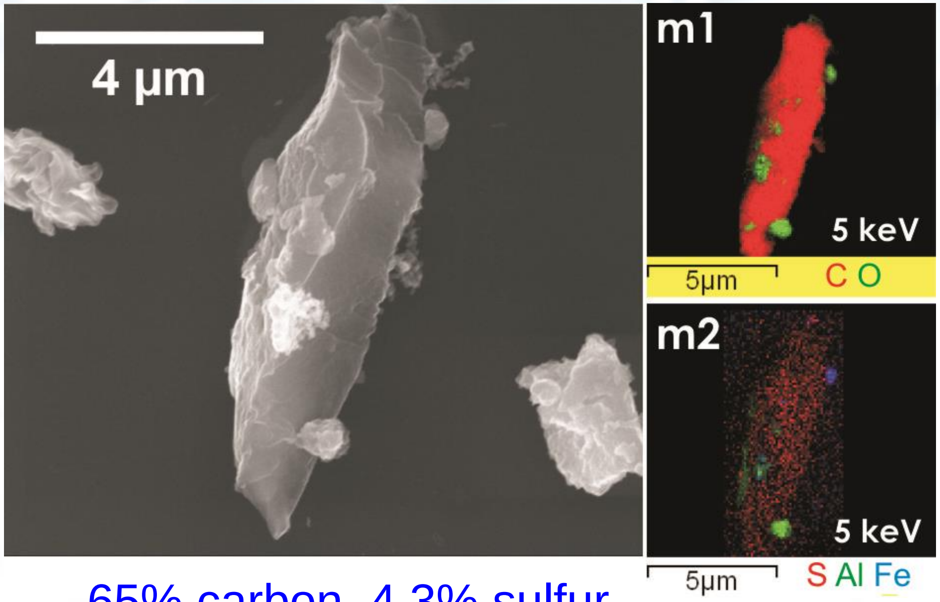




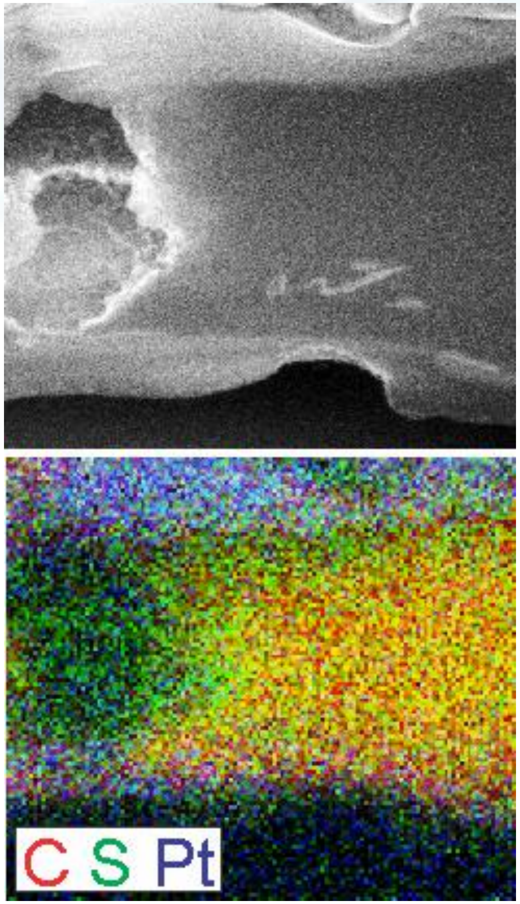




Optical Behavior of an Individual Particle



65% carbon, 4.3% sulfur

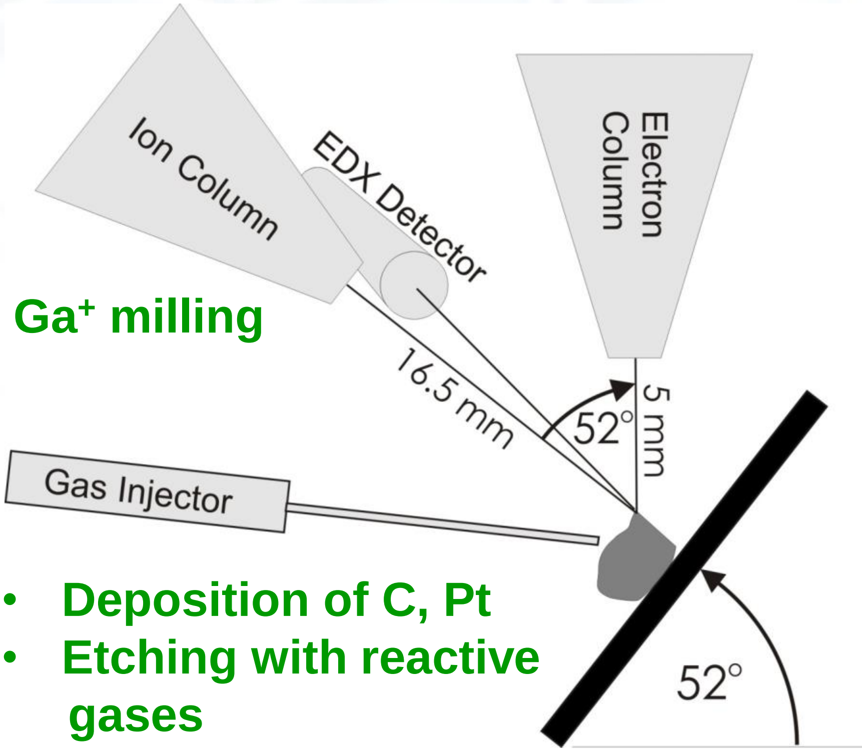


Is sulfur on the surface, e.g. $(NH_4)_2SO_4$, or throughout particle as in tire wear?

Single-scattering albedo (scattering/extinction ratio)

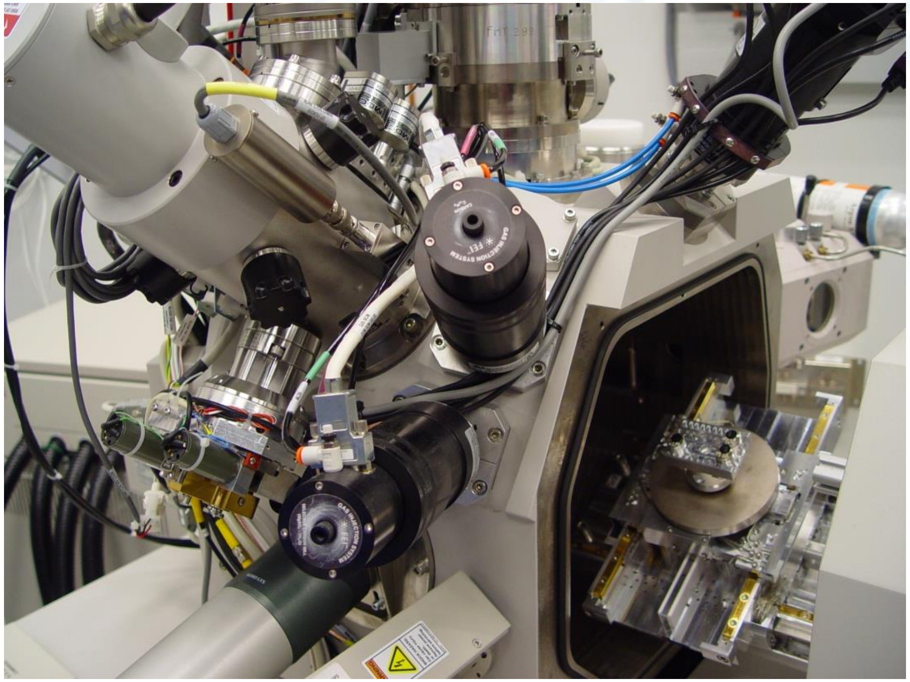
- Tire wear particle: 0.54
- If assume sulfate shell/soot core: 0.49
- If assume sulfate shell/graphite core: 0.54
    - But, backscattering 37% higher than tire wear!

Focused Ion-Beam SEM

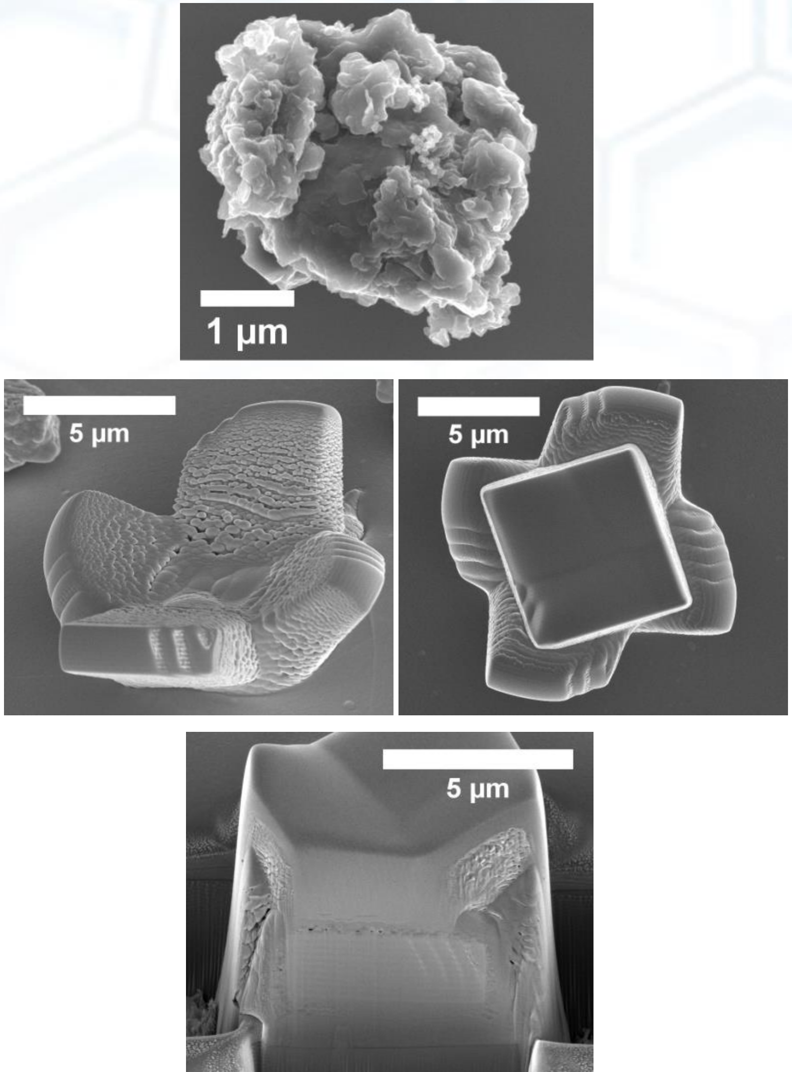


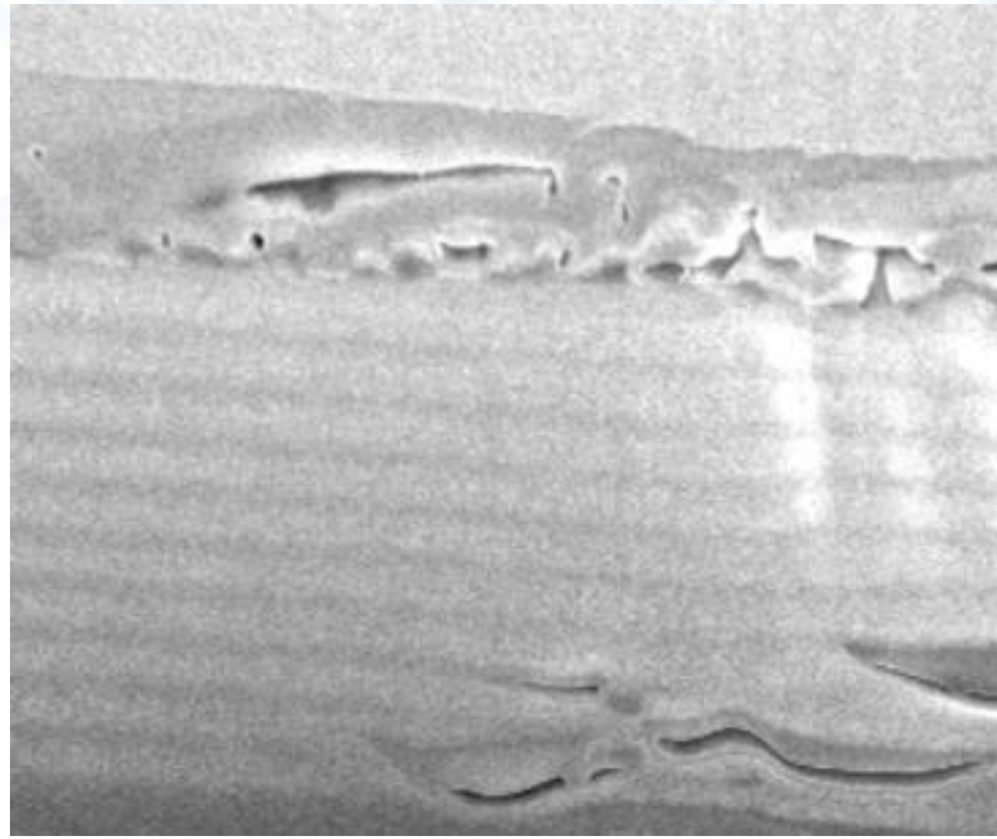
Ga^{+} milling

- **Deposition of C, Pt**
- **Etching with reactive gases**

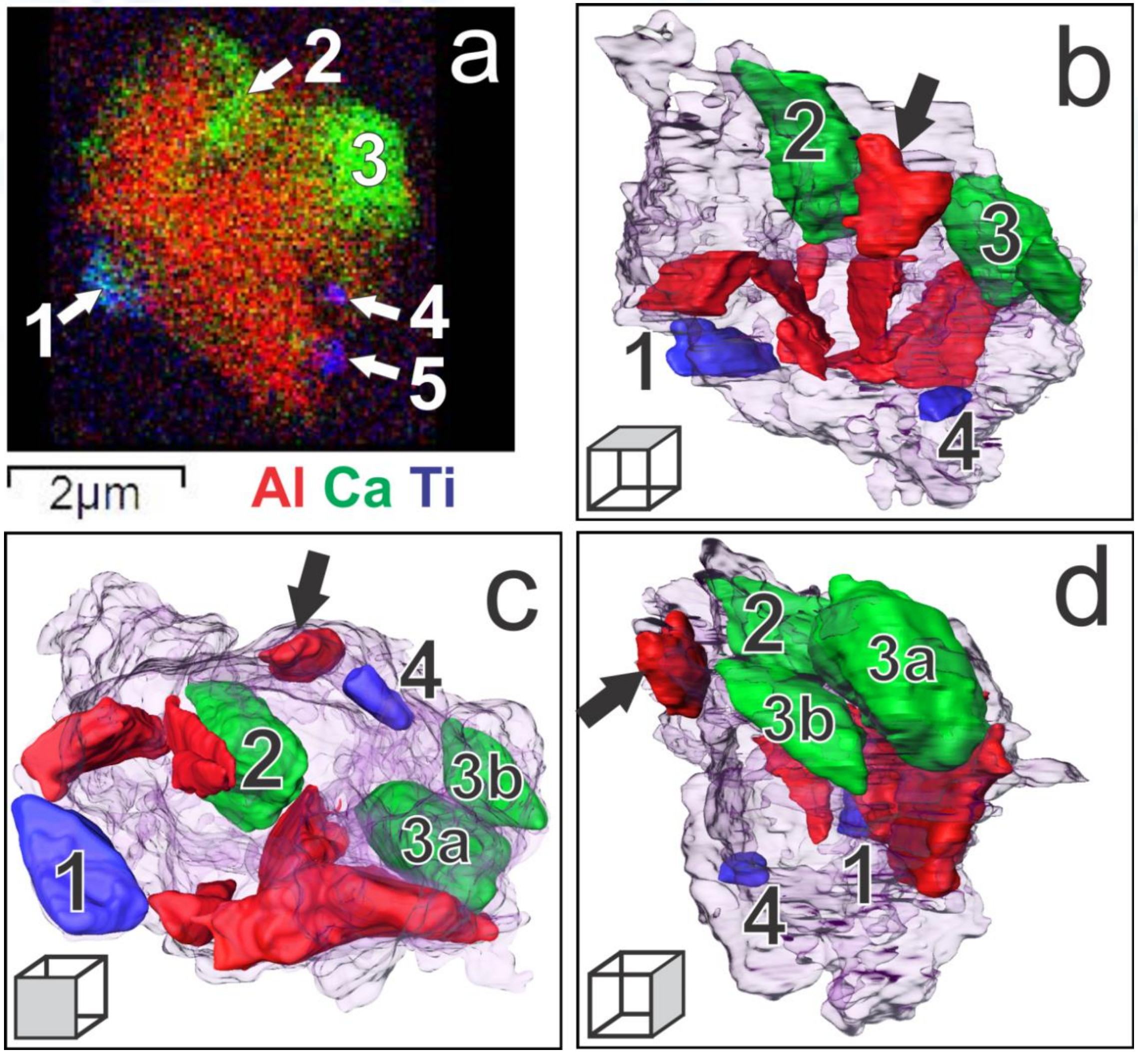


FIB Tomography



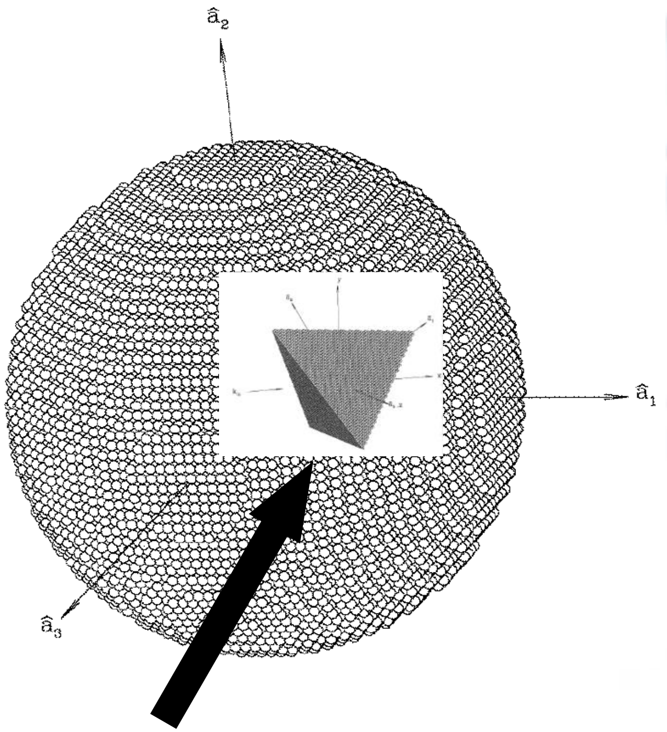


Particle Internal 3-D Structure



Optical Modeling: Discrete Dipole Approximation*

- Particle partitioned into *M* dipole 'points'
- Each dipole excited by *superposition* of external field and other dipoles' fields
- Total scattered field is numerical solution of *M* partial fields

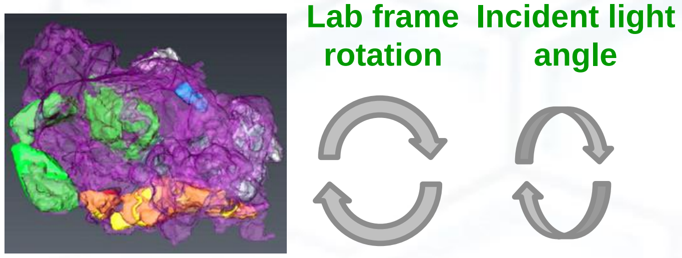


Advantages
- Ideal for arbitrarily-shaped, heterogeneous, and optically-anisotropic particles
- Physical model relatively simple
- Code availability and documentation: DDSCAT 6.0 (Princeton Univ.)

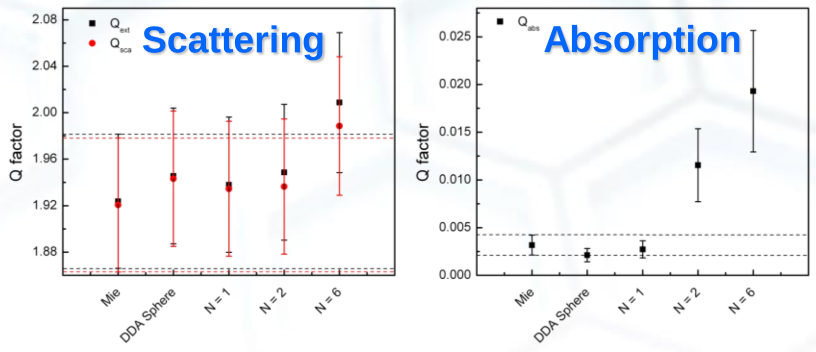
Must specify dipole locations and compositions (dielectric constant or refractive index).

*Draine, B.T and P.J. Flatau, 1994, *J. Opt. Soc. Am, 11*, 1491-1499.

Optical Model From Particle 3-D Reconstruction

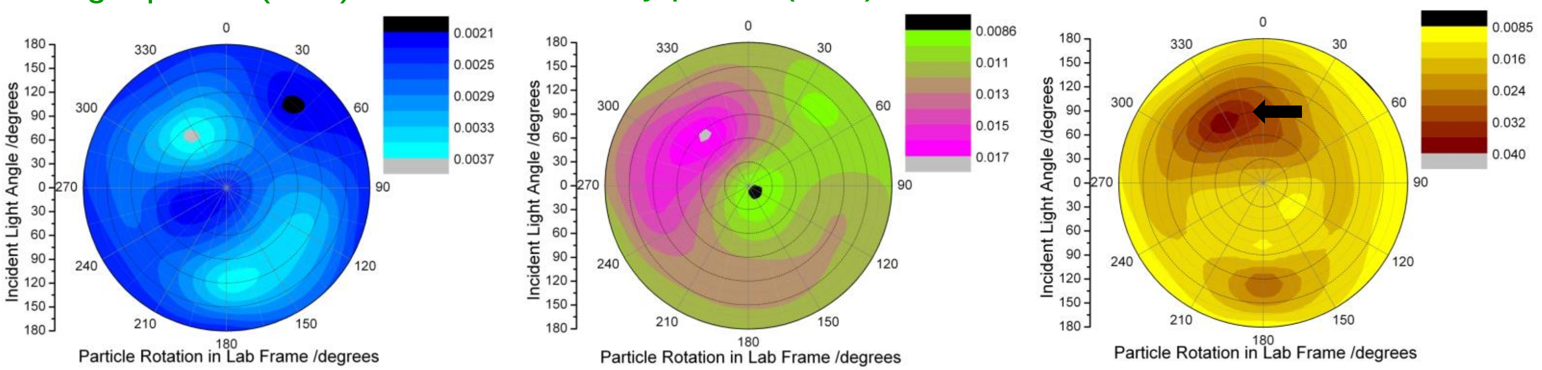


Efficiency Factors

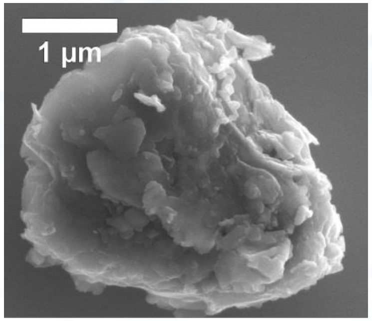


Absorption Asymmetry

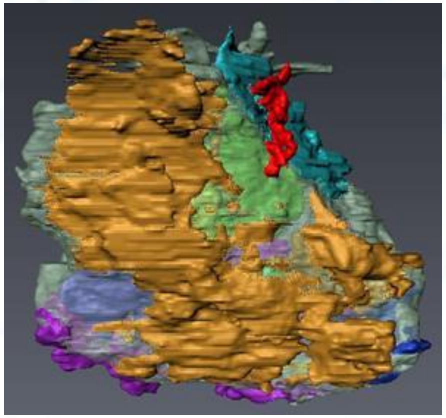
Single phase (N=1) Binary phase (N=2) "All" phases (N=6)



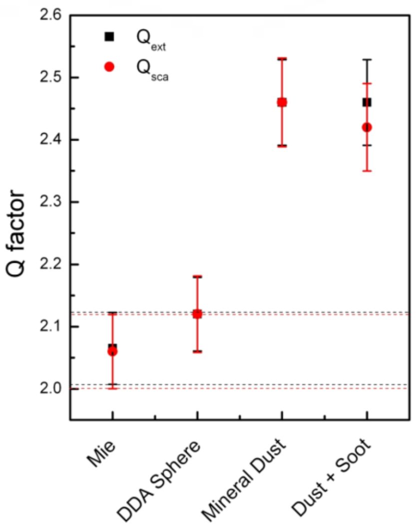
Effect of a Soot on a Mineral Particle

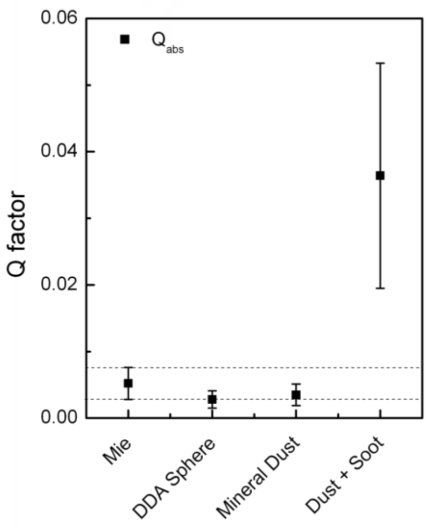


FIB Tomography/3D



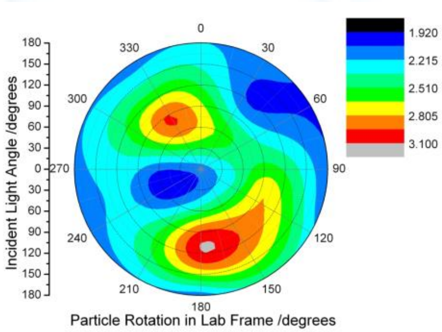
Scattering/Absorption Efficiency



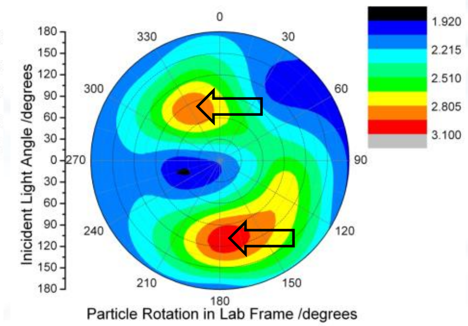


Scattering Asymmetry

Mineral Dust

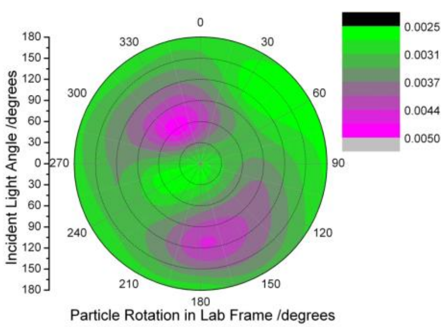


Mineral Dust + Soot

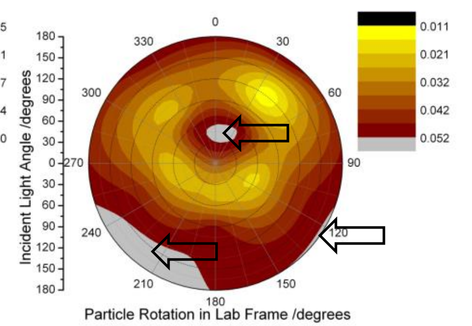


Absorption Asymmetry

Mineral Dust



Mineral Dust + Soot



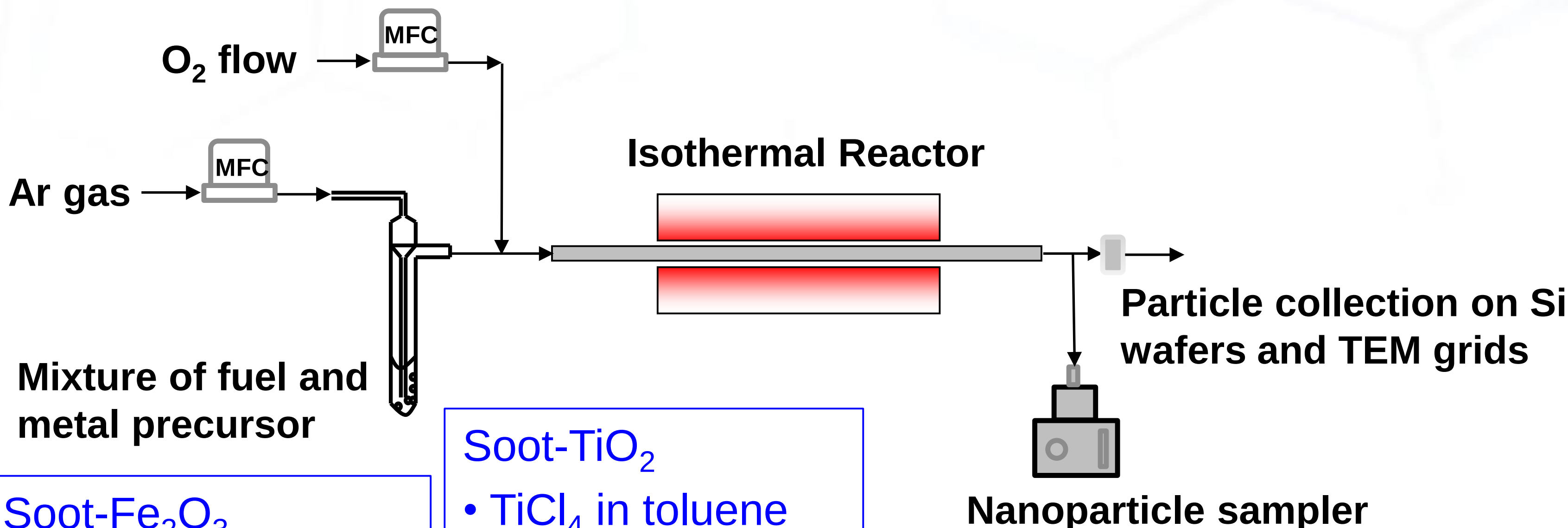
Lab-Generated Mixed-Phase Particles

Purpose

- Quantify variation in absorption and scattering in ambient particles based on lab “proxies”
- Reference materials for calibrating optical measurements

Experimental Goals

- Separate absorbing and scattering phases
- Control particle size, shape/morphology, and phase placement

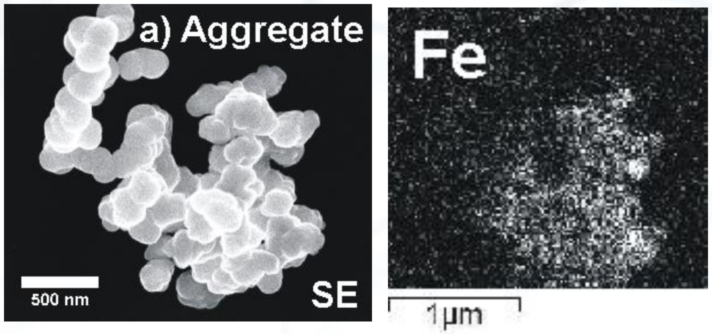


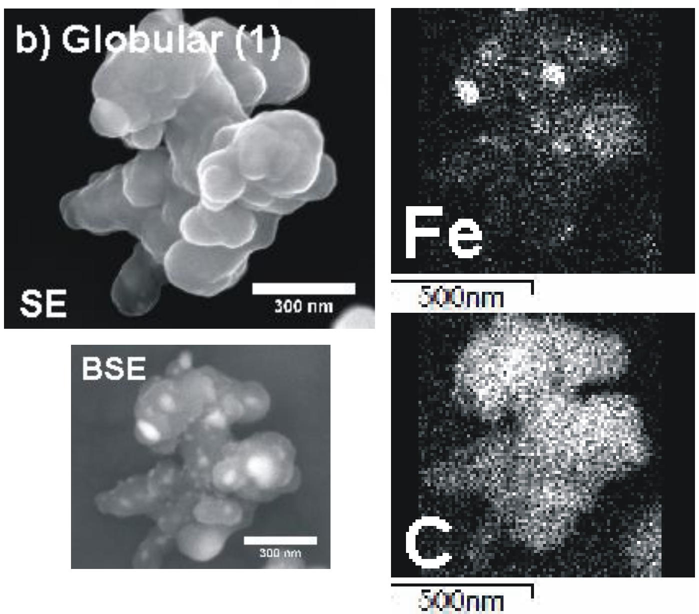
Soot-Fe_2O_3
- $Fe(CO)_5$ in toluene

Soot-TiO_2
- $TiCl_4$ in toluene
- $TiCl_4$ in isooctane

Soot-Fe_2O_3

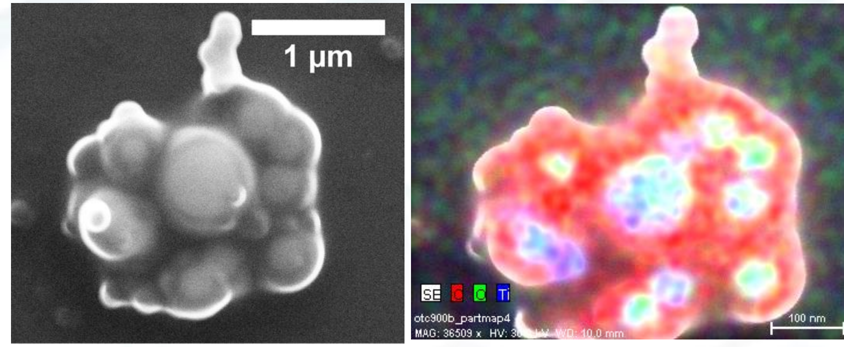
$Fe(CO)_5$ in Toluene, >1000 ^oC



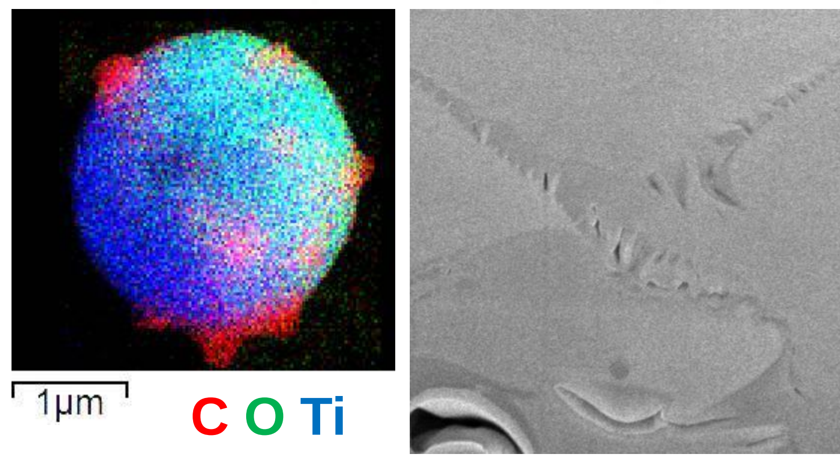


Soot-TiO_2

$TiCl_4$ in Isooctane, 900 ^oC



$TiCl_4$ in Toluene, 900 °C



Paradigm for Binary-Phase Particulate Reference Materials

	Strongly Scattering		Weakly Scattering	
Strongly Absorbing	Inclusion(s) + Matrix	Candidate: Soot + TiO_2	Inclusion(s) + Matrix	Candidate: Fe_2O_3 + Soot
	Core / Shell	Candidate: Soot / $(NH_4)_2SO_4$	Core / Shell	Candidate: Soot / PAH(e.g. fluorene)
	Core / Shell	Candidate: TiO_2 / Soot (High temp TiO_2 synthesis followed by lower temp coating with soot)	Core / Shell	Candidate: Fe_2O_3 / soot (High temp Fe_2O_3 synthesis followed by lower temp coating with soot)
Weakly Absorbing	Inclusion(s) + Matrix	Candidate: Fe_2O_3 + TiO_2		
	Shell / Core	Candidate: PAH(e.g. perylene) / TiO_2		
	Core / Shell	Candidate: TiO_2 / PAH (e.g., perylene) (High temp TiO_2 synthesis followed by lower temp coating with PAH)		

	R.I.	k
Soot	1.95	0.79
TiO_2	2.85-255	~0
Fe_2O_3	2.3-2.18	0.15-0.07
$(NH4)_2SO_4$	1.53	~0
Perylene (sub. 350-400°C)	1.7	0.26
Fluorene (b.p. 293°C)	1.6	

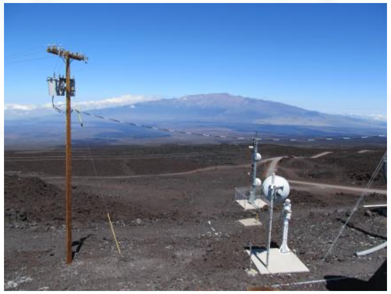
Future Directions

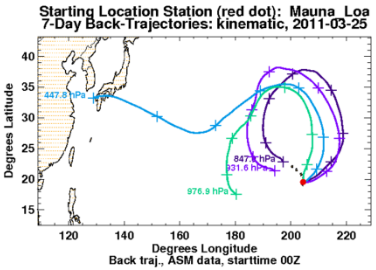
- Comprehensive assessment of natural variation in solar absorption and scattering for atmospheric dust:

  Variation assessed for
    - Regions
    - Seasons
    - Urban vs. rural
    - ***Aged aerosol***

- Suite of lab-generated particles with mixed absorption and scattering phases for optical measurement calibration
    - Size resolved
    - Morphology controlled

EPA Collaboration on Asian Dust





Thank you for your attention!